ANAEROBIC-AEROBIC TREATMENT OF VEGETABLE TANNING WASTE

Abstract

Vegetable tanning waste can be treated effectively on a laboratory scale by a combination of an anaerobic contact reactor followed by a complete-mix aerobic reactor. The 28.7 liter anaerobic reactor is constantly stirred and maintained at 37°C. A settling tank follows to permit sludge recycling. The aerobic reactor contains 22.6 liters of microorganisms, which are suspended by the flow of air. Waste aerobic sludge is recycled back to the anaerobic reactor for digestion.

With a hydraulic retention time of 58 hr. and a loading of 2.5-5.0 g TCOD/day, an average TCOD removal of 90 percent was obtained (corrected for $S^{=}$). The anaerobes produced an average of 0.161 liters CH_4/g TCOD removed. The CH_4 can potentially be recovered and used to maintain the temperature of the anaerobic reactor.

Introduction

A bench-scale anaerobic contact reactor for the treatment of category I chrome tannery waste has been developed in our laboratory (1-4). The reactor was routinely capable of removing about 60 percent of the applied total chemical oxygen demand (TCOD); when the anaerobic effluent was fed to an aerobic reactor for polishing, the efficiency of the system increased to 85 percent. The CH_4 produced by the anaerobes could be recovered and used for heating the reactor. The reactor demonstrated these capabilities despite normally toxic $S^{=}$ levels of over 200 mg/l and chromium levels of 30 mg/l.

After completing research on treating waste streams from chrome tanning operations, the performance of the same anaerobic-aerobic combination was studied using vegetable tanning waste (VTW) as the feed.

Materials and Methods

Reactors

A schematic diagram of the system is shown in Figure 1. The anaerobic reactor is a glass cylinder 12 in. ID, 18 in. high, and containing 28.7 l of suspended anaerobic sludge. The air-tight cover has provisions for stirring, heating, feeding, sampling, and gas collection. The sludge is suspended by a stainless steel stirrer, driven at 60 rpm by a 0.05 HP electric motor. The impeller consists of two 2-in. square blades pitched at 45° and suspended 4.5 in. from the bottom of the reactor. The mother liquor is maintained at 37°C by an immersion heater located in a silicone-filled test tube suspended from the cover. Two stainless steel tubes extending to within 6 in. of the reactor bottom are mounted in the cover. One of these is used for feed (F) and the other for withdrawing liquid samples. Gas samples are obtained by a hypodermic syringe through a septum located in the cover. Gas volume is measured by a wet tip gas meter.

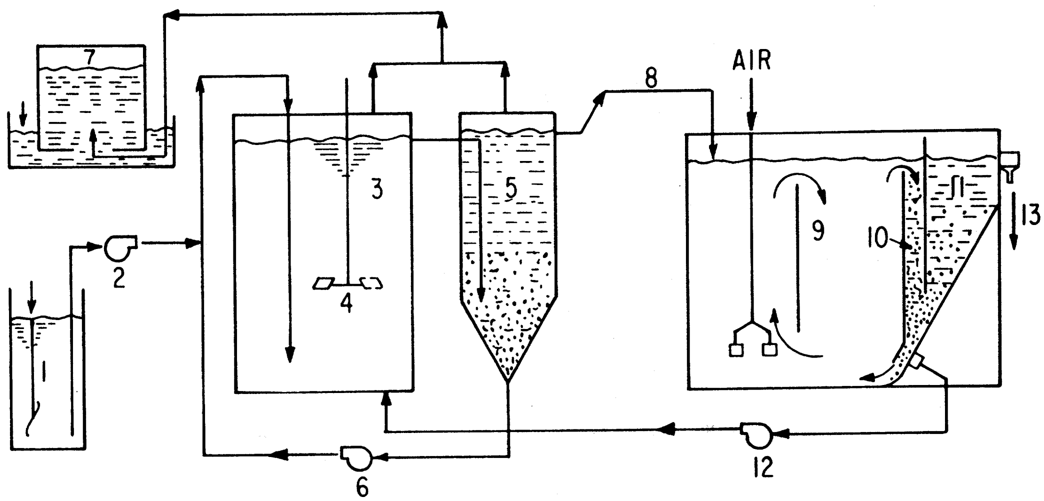

FIGURE 1. — Schematic Diagram of the Treatment System.

1. Feed Tank
2. Feed Pump
3. Anaerobic Reactor
4. Stirrer
5. Settling Tank
6. Return Sludge Pump
7. Gas Collector
8. Primary Effluent
9. Aeration Tank
10. Settling Zone
11. Clarification Tank
12. Waste Sludge Pump
13. Final Effluent

A horizontal tube 0.5 in. ID and 15 in. from the bottom connects the reactor to the settling tank, a glass cylinder 6 in. ID, 18 in. high, and holding 6.3 l. As the effluent leaves the reactor it flows into the settling tank and down through a stainless steel tube to within 4 in. of the bottom. The bottom is cone-shaped to collect settleable sludge which is recirculated back to the reactor at 70 ml/min. This removes the need to waste the sludge. The settled primary effluent (PE) exits through an opening opposite the entrance port, passes through a vapor lock to prevent escape of gas, and drains into the aerobic reactor.

The open-topped, complete-mix aerobic reactor is 20 in. high, 14 in. wide, and 6 in. deep, and consists of three compartments: a 12.9 l aeration tank, a 6.2 l settling zone, and a 3.5 l clarification tank. The solids in the aeration tank are suspended by an air flow of 5 l/min. The contents of this reactor are not stirred, except through aeration, or heated. Waste sludge is pumped from the bottom of the settling zone and into the anaerobic reactor at a rate of 70 ml/hr. The overflow from the final tank is the final effluent (FE).

Anaerobic sludge from a municipal plant was used in the start-up of the anaerobic system (AS). At that time, the feed consisted of glucose and dilute tannery waste. The AS had been operating for 3½ years prior to the start of this study using various tannery waste streams and feed rates ranging from 10 to 40 l/day. The aerobic reactor was used only during the final year. The VTW in this study consisted of combined equalization effluent supplied by Clearfield Tanning Company, Clearfield, PA*. The beamhouse waste (BW) came from various tanneries. The influent, with a TCOD concentration between 2000 and 5000 mg/l, is continuously added to the system at the rate of 24 l/day. The total hydraulic retention time is 58 hr.

Methods

The total chemical oxygen demand (TCOD) was measured by the culture tube method of Knechtel (5). Correction for sulfide ($S^=$) was made by taking twice the sulfide concentration and subtracting this number from the TCOD concentration. Gas composition was measured with a Hewlett-Packard Model 5734A gas chromatograph (column: 6 ft × 3/16 in. aluminum; packing: molecular sieve; sample volume: 0.5 ml; carrier: 20 ml He/min; temperature programing: 120 to 190°C at 32°C/min; detector: thermal conductivity). Total solids (TS), suspended solids (SS), and volatile suspended solids (VSS) were determined by procedures in *Standard Methods*, 14th edition (6). Sulfide was analyzed titrimetrically by oxidation with $K_3Fe(CN)_6$ (7). Ammonia levels were measured with an Orion Model 95-10 specific ion electrode.

Bioassays

Bioassays were performed in 160-ml borosilicate glass serum bottles. Each bottle was filled with a gas mixture consisting of 70 percent N_2 and 30 percent CO_2 and sealed with a butyl rubber stopper and aluminum seal. Combinations of BW, VTW, and sludge from the AS were prepared and 100-ml aliquots were then syringed into each bottle, taking care to avoid the introduction of air. The bottles were stored in a 37°C incubator. Gas production in each bottle was monitored by piercing the stopper with a syringe needle and noting the displacement of the syringe barrel. The sample in the syringe was then injected into the gas chromatograph.

Results and Discussion

Table I shows the COD concentrations of the ingredients in each of the bottles in the bioassays, along with the total volume of CH_4 that each sample produced during the 16-day course of the study. It can be concluded that COD destruction and CH_4 production were seriously inhibited when the ratio of vegetable waste COD to sludge VSS was greater than 0.20. The anaerobic in the reactor would thus be expected to suffer the same deleterious effects if the feed were suddenly changed to 100 percent VTW. The influent was gradually converted from BW to VTW over the course of 24 days, during which the anaerobes became acclimated to the new type of feed. The COD to VSS ratio was approximately 0.15 in that period. The ratio sometimes went above 0.2 after the conversion was complete, but the reactor performance was not hindered.

TABLE I

SAMPLE COMPOSITIONS AND CH_4 PRODUCED

mg/l COD from VTW	mg/l COD from BW	Ratio of VTW COD to Sludge VSS	Total ml CH_4
	5,000 mg/l VSS Sludge		
3000	0	0.6	0
2000	1125	0.4	0.1
1200	2025	0.24	0.8
400	2925	0.08	42.8
0	3375	0	50.3
	10,000 mg/l VSS Sludge		
2000	0	0.20	30.0
1600	450	0.16	37.7
1200	900	0.12	38.1
800	1350	0.08	48.8
0	2250	0	44.9

The average TCOD removal by the reactors was virtually unaffected during the phase-in of VTW in the influent, although CH_4 production was nearly halved (Table II). Production of CH_4 by anaerobic reactors is much more sensitive to changes in the influent than TCOD removal (1). After the changeover was completed, the TCOD removal efficiency of the AS was found to be slightly lower than before, but the efficiency of aerobic reactor increased, leading to a TCOD removal of 90%. This is quite high compared with other methods of tannery waste treatment (8, 9).

TABLE II

AVERAGE TCOD REMOVALS AND CH_4 PRODUCTION WITH VARIOUS INFLUENTS

	BW	BW + VTW	VTW
Days used	73	24	45
g TCOD removed by AS/day	96.4	76.3	45.6
% TCOD removal			
by AS	72	73	63
overall	83	79	90
1 CH_4 produced			
per day	18.5	8.05	7.33
per g TCOD removed	0.192	0.105	0.161

The CH_4 production, 0.161 l/g of TCOD removed, came to within 84 percent of the value obtained with BW influent. The 7.33 l CH_4 produced per day has a potential energy of 2.62 x 10^5 J. If the CH_4 is recovered, it could be used to offset some of the energy costs of the system.

The $S^=$ levels in the anaerobic reactor and PE were always higher than those in the influent due to the breaking of the disulfide linkages in the keratin present. The anaerobes produced CH_4 in spite of the $S^=$, to which they had become acclimated in earlier studies. The aerobic reactor presumably oxidized most of the sulfide to sulfate. The ammonia levels in the F, PE, and FE were all found to lie between 50 and 62 mg/l. The FE level is not low enough to meet EPA guidelines, which would necessitate a denitrification step.

The pH of the VTW was sufficient to keep the pH of the reactors above 7.0, thus preventing significant evolution of H_2S. The pH of the FE was within the range of 7.0-8.5. The same pH behavior had been observed with BW influent.

With VTW influent, solids present in the FE were lower than when BW influent was used (Table III). This is probably due to lower solids levels in the VTW. Since the aerobic sludge was recycled back into the anaerobic reactor, the solids levels in the FE were lower than they would have been otherwise.

Despite a hydraulic retention time of only 58 hr, the anaerobic-aerobic system performed well. There is every indication that the process would be equally effective if it were scaled up

TABLE III

VALUES OF VARIOUS PARAMETERS (IN mg/l) WITH BOTH TYPES OF INFLUENT

	BW Influent			VTW Influent		
	F	PE	FE	F	PE	FE
TCOD	4590	1270	780	2960	1110	290
$S^=$	130	300	54	21	94	14
pH	10.7	7.3	8.1	7.9	7.3	7.5
TS	11600	7720	7280	8200	7800	7000
SS	—	780	170	—	130	30
VSS	—	410	100	—	65	15

to handle the full load from a tannery. The anaerobic reactor would have to be maintained at 37°C for full efficiency, but the CH_4 recovered could be used in conjunction with heat exchangers to offset some of this requirement. The system compares favorably with published results of other bench scale tannery waste treatment processes, none of which had TCOD removal or CH_4 production as high (9).

Conclusions

An anaerobic-aerobic system which had been used to treat tannery beamhouse waste has also been found to be successful in treating vegetable tanning waste. Its attributes include a 90 percent reduction in applied TCOD and methane production which is high enough to be of value in reducing energy costs. In addition, the need to waste some of the sludge produced was prevented by a recycle system. A period of 24 days was necessary to acclimate the anaerobes to the VTW.

References

1. Tunick, M. H., Friedman, A. A. and Bailey, D. G. *Mid-Atlantic Indus. Waste Conf. Proc.*, **13**, 197 (1981).
2. Bailey, D. G., Tunick, M. H. and Kuzma, M. A. *Mid-Atlantic Indus. Waste Conf. Proc.*, **14**, 202 (1982).
3. Bailey, D. G., Tunick, M. H., Friedman, A. A. and Rest, G. B. *Indus. Waste Conf. Proc.* **38**, 673 (1984).
4. Cooper, J. E., Moore, J. H. and Bailey, D. G. *JALCA* (in review).
5. Knechtel, J. R. *Water and Pollution Control*, May-June 1978, p. 25.
6. "Standard Methods for the Examination of Water and Wastewater," 14th ed., Washington, DC, APHA, 1976.
7. Booth, H. *J. Soc. Leather Trades Chemists,* **40**, 238 (1956).
8. U.S. Environmental Protection Agency, "Leather Tanning and Finishing Point Source Category Effluent Limitations Guidelines, Pretreatment Standard, and New Source Performance Standards," *Federal Register*, **44**, 38746 (July 2, 1979).
9. Young, K. S. *M.S. Thesis* (Syracuse, NY: Syracuse Univ., Dept. of Civil Engineering, 1980).

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